Chapter 10 - **THE SANS TECHNIQUE**

1. RECIPROCAL SPACE

Small-Angle Neutron Scattering (SANS) is a technique of choice for the characterization of structures in the nanoscale size range (Hammouda, 1995). This covers structures from the near Angstrom sizes to the near micrometer sizes. How small are the small angles? They are typically from 0.2 º to 20 º and cover two orders of magnitude in two steps. A low-Q configuration covers the first order of magnitude (0.2 º to 2 º) and a high-Q configuration covers the second one (2 º to 20 º). The scattering variable is defined as $Q = (4\pi/\lambda) \sin(\theta/2)$ where λ is the neutron wavelength and θ is the scattering angle. Within the small-angle approximation, Q simplifies to $Q = 2\pi\theta/\lambda$. The SANS scattering variable Q range is typically from 0.001 $Å^{-1}$ to 0.45 $Å^{-1}$. This corresponds to d-spacings from 6,300 Å down to 14 Å.

Scattering measurements are performed in the Fourier (also called reciprocal) space, not real space like microscopy. For this, scattering data have to be either inverted back to real space or fitted to models describing structures in reciprocal space. Scattering methods measure correlation functions. These are not the Fourier transform of the density of inhomogeneities within the sample. They are the density-density correlation functions instead. It should be noted that because of this, the "phase" information is completely lost. It is not possible to reconstruct a complete image of the sample structure by scattering from one sample. Trying to recover phase information is complicated and involves measuring a series of samples with identical structures but different contrasts.

2. COMPARING SANS TO OTHER TECHNIQUES

The advantage of SANS over other small-angle scattering methods (such as small-angle x-ray or light scattering) is the deuteration method. This consists in using deuterium labeled components in the sample in order to enhance their contrast. This is reminiscent of contrast variation in microscopy whereby the level of light incident upon a sample is varied using a diaphragm. SANS can measure either naturally occurring contrasts or artificial contrasts introduced through deuteration. Labeling is difficult to achieve with x-rays (SAXS) since this involves heavy atom labels that change the sample drastically. SANS can measure density fluctuations and composition (or concentration) fluctuations. SAXS can measure only density fluctuation. The deuteration method allows this bonus.

SANS is disadvantaged over SAXS by the intrinsically low flux of neutron sources (nuclear reactors or spallation sources using cold source moderators) compared to the orders of magnitude higher fluxes for x-ray sources (rotating anode or synchrotrons). Neutron scattering in general is sensitive to fluctuations in the density of nuclei in the sample. X-ray scattering is sensitive to inhomogeneities in electron densities whereas light scattering is sensitive to fluctuations in polarizability (refraction index).

Microscopy has the advantage that data are acquired in direct (real) space whereas scattering methods (such as SANS) measure in reciprocal space. Electron microscopy (EM) and SANS are complementary methods. EM is applied on very thin samples only, it cannot measure samples at different concentrations and temperatures directly, and the observed images are a 2D projection. SANS can do all these things but cannot produce an image in real space.

SANS data analysis is performed at many levels. The initial level consists of "follow the trends" type of approach using standard plot methods. The next level uses nonlinear least squares fits to realistic models. The final trend makes use of sophisticated ab-initio or "shape reconstruction" methods in order to obtain insight into the structure and morphology within the investigated sample. Oftentimes, it takes independent information obtained from other methods of characterization to obtain a thorough understanding of SANS data because "most SANS data look alike". SANS is not known for abundance in scattering peaks (unlike single-crystal diffraction, Nuclear Magnetic Resonance, Infra-Red spectroscopy, etc) but enough features (i.e., "clues") are available. Available models describe scattering from compact shape objects in dilute or concentrated systems as well as "non-particulate" scattering such as in the case of gel-like or porous media. SANS has been used for single-phase as well as multi-phase systems. Phase transitions have been investigated as well as the thermodynamics of demixing.

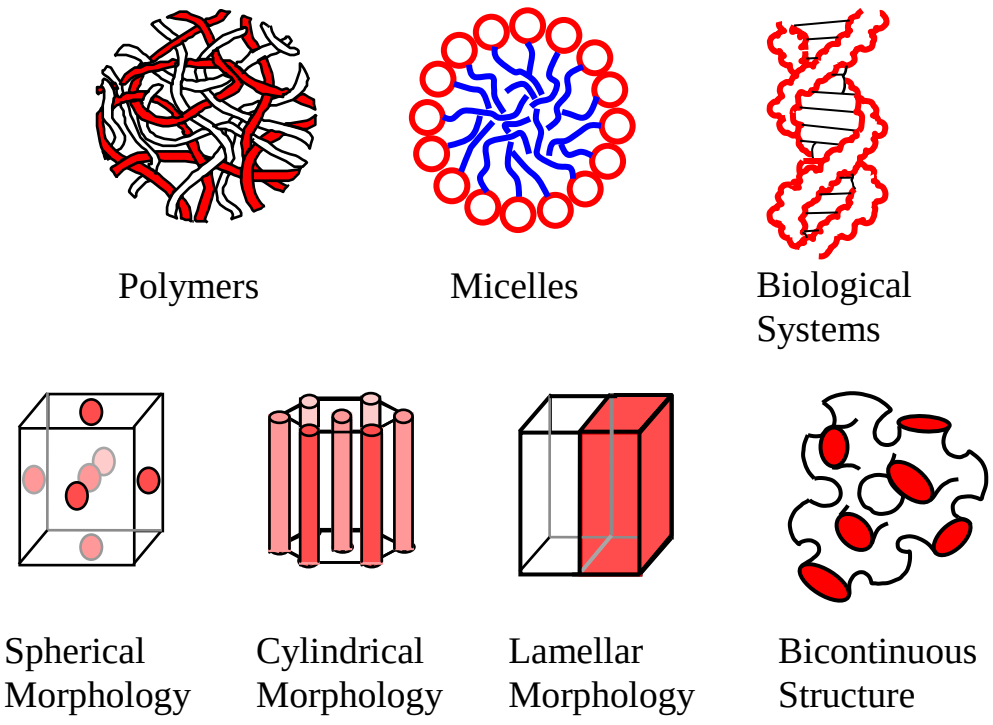

Figure 1: Various classes of samples and morphologies investigated by SANS.

3. THE SANS TECHNIQUE

SANS involves the basic four steps used in all scattering techniques: monochromation, collimation, scattering and detection. Monochromation is performed mostly using a velocity selector. Collimation is preformed through the use of two apertures (a source aperture and a sample aperture) placed far (meters) apart. Scattering is performed from either liquid or solid samples. Detection is performed using a neutron area detector inside an evacuated scattering vessel. The large collimation and scattering distances make SANS instruments very large (typically 30 m long) compared to other scattering instruments.

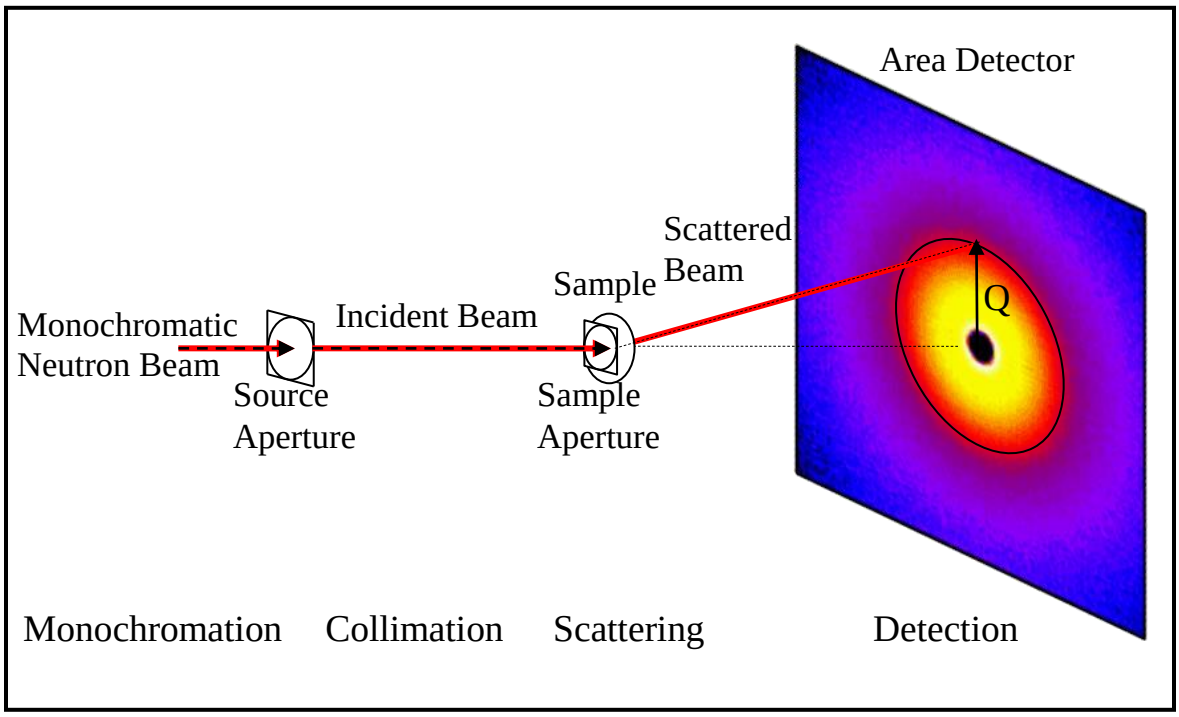

Figure 2: This figure represents the schematics of the SANS technique. It is not to scale with vertical sizes in centimeters whereas horizontal distances are in meters.

The SANS technique has been an effective characterization method in many area of research including Polymers, Complex Fluids, Biology, and Materials Science. Other areas such as magnetism also benefited from SANS. SANS instruments have been essential components for any neutron scattering facility for almost three decades. They provide the main justification for growth and are highly oversubscribed. New sample environments have given new momentum to the technique. These include in-situ shear cells, flow cells and rheometers, pressure cells, electromagnets and superconducting magnets, vapor pressure cells, humidity cells, in-situ reaction cells, etc. New advances in electronics, data handling methods and computers have made SANS a sophisticated "user friendly" characterization method for the non-experts and for "routine" characterization as well as cutting edge research.

4. THE MEASURED MACROSCOPIC SCATTERING CROSS SECTION

Consider a simple scattering system consisting of globular (think spherical) inhomogeneities in a matrix (think solvent). If this system is assumed to be incompressible, the SANS coherent macroscopic scattering cross section (scattering intensity in an absolute scale) can be modeled as:

$$\frac{d\Sigma_c(Q)}{d\Omega} = \left(\frac{N}{V}\right) V_P^{\,2} \Delta\rho^2 P(Q) S_I(Q). \qquad (1)$$

(N/V) is the number density of particles, V_P is the particle volume, $\Delta\rho^2$ is the contrast factor, P(Q) is the single particle form factor and $S_I(Q)$ is the inter-particle structure factor. Note that P(Q) and $S_I(Q)$ are normalized as follows: $P(Q\rightarrow 0) = 1$, $P(Q\rightarrow\infty) = 0$ and $S_I(Q\rightarrow\infty) = 1$. $S_I(Q)$ has a peak corresponding to the average particle inter-distance (the so-called coordination shell) in the case of "concentrated" system where the particle inter-distance is of the same order as the particle size. The inter-distance is much larger than the particle size for "dilute" system.

The incoherent scattering cross section $d\Sigma_i/d\Omega = \Sigma_i/4\pi$ is a constant (Q-independent) background to be added to the coherent scattering level. Its contribution is mostly from hydrogen scattering in the sample.

5. NEUTRON CONTRAST CONDITIONS

Consider a scattering system made of spheres in a solvent background. The following figures consider four types of contrast conditions: (1) finite contrast, (2) zero contrast for two component systems, (3) multiple contrasts and (4) the scattering length density match condition for three component systems. The scattering length density match condition corresponds to zero contrast for the blue spheres.

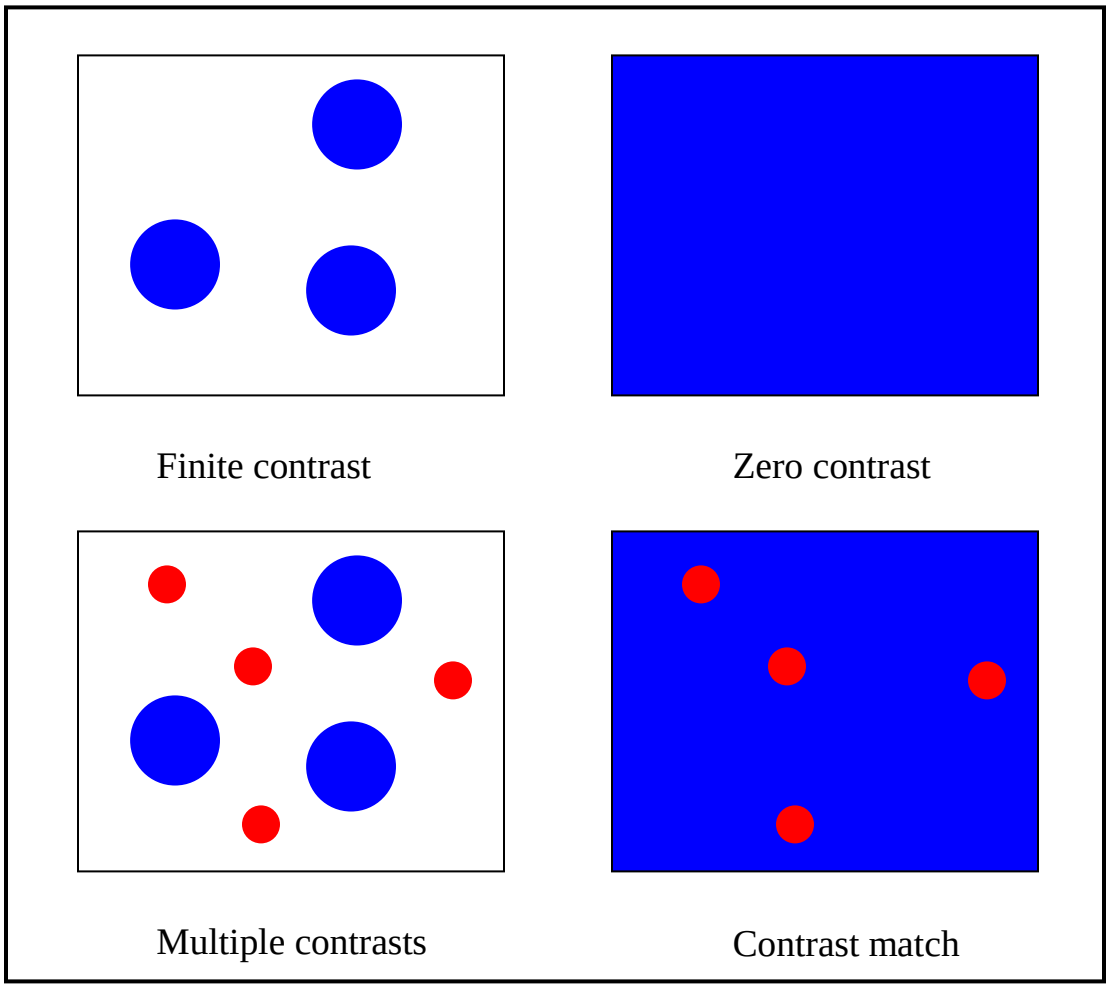

Figure 3: Various contrast conditions.

6. THE PHASE PROBLEM

The so-called "phase problem" affects all scattering methods because measurements are performed in reciprocal (Fourier) space. In order to explain the issue, let us consider the simple case of a scattering medium (think solvent) of scattering length density ρ_g (think "grey" color), and two set of structures, one comprised of "white" spheres of scattering length density ρ_w and one comprised of "black" spheres of scattering length density ρ_b. Assume that the white and black spheres are identical except for their scattering length densities (i.e., "color" as appearing to neutrons) that are opposite. Also assume that the white spheres are hydrogenated ($\rho_w < \rho_g$) and the black spheres are deuterated ($\rho_b > \rho_g$). Microscopy is sensitive to the following differences $\rho_w-\rho_g <0$ and $\rho_b-\rho_g >0$ whereas scattering methods are sensitive to the following "contrast factors" $(\rho_w-\rho_g)^2 > 0$ and $(\rho_b-\rho_g)^2 >0$. Both are positive and therefore appear the same. In order to defeat the phase problem, a second sample is necessary whereby the scattering length density of the

solvent matches that of the black spheres for example ($\rho_g = \rho_b$). In this case the black spheres will be invisible and the white spheres will be distinct.

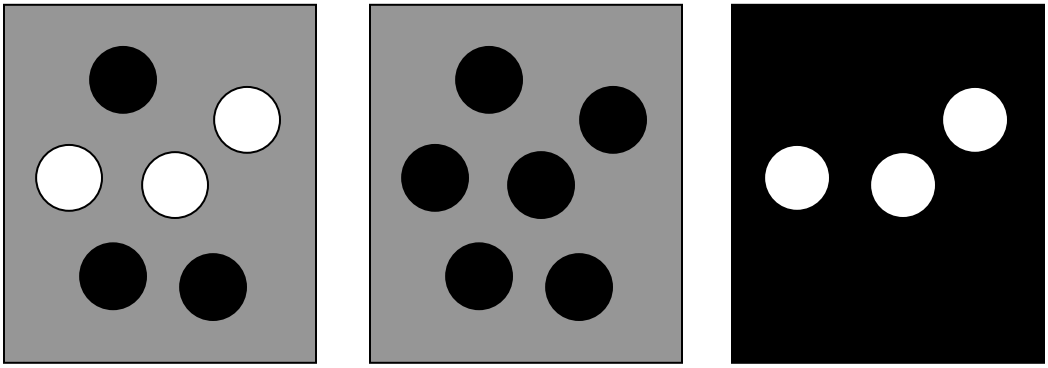

Figure 4: Microscopy sees the white spheres and the black spheres as distinct. Scattering with one sample sees the black spheres and the white spheres as similar. A second sample (where the scattering length density of the solvent matches that of the black spheres) shows the white spheres.

This is an oversimplified view of the more complex phase problem. The central aspect of the phase problem comes from the square nature in the form factor $P(Q) = F^2(Q)$. Consider the case of scattering from a sphere of radius R for which $F(QR) = 3j_1(QR)/QR$ where $j_1(QR)$ is the spherical Bessel function given by $j_1(QR) = \sin(QR)/(QR)^2 - \cos(QR)/QR$. In order to obtain the variation of F(QR) from P(QR), one needs more information in order to reconstruct the negative values of F(QR). Here also, scattering from one sample does not suffice.

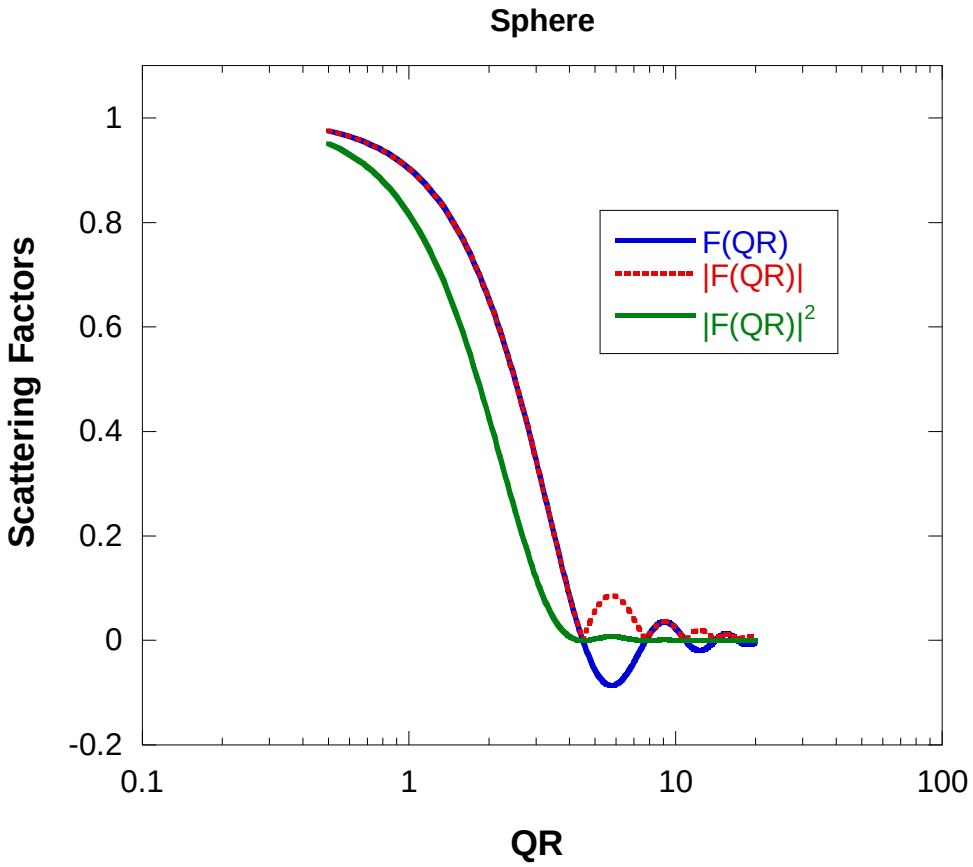

Figure 5: Comparison of the three scattering factors for a sphere F(QR, |F(QR)| and $P(QR) = |F(QR)|^2$.

The phase problem is resolved for x-ray single crystal diffraction by including heavy atoms in the structure and in neutron reflectometry and SANS by preparing samples with the same structures but different deuteration schemes.

REFERENCE

B. Hammouda, "SANS from Polymers Tutorial", NIST Center for Neutron Research Report (1995)

QUESTIONS

1. What is reciprocal space?
2. What is the phase problem? How to go around it?
3. What are the four basic steps involved in the concept of the SANS instrument?
4. What is the range of scattering angles used in SANS?
5. What are typical sample environments for in-situ SANS measurements?

6. What are the major SANS research areas?
7. Why are SANS instruments bigger than SAXS instruments?

ANSWERS

1. Reciprocal space is the Fourier transform space.
2. The phase problem is due to the fact the scattering contrast factor involves the square of the difference in the scattering length densities so that differences that are opposite in sign show the same contrast. The phase problem is resolved by preparing more than one sample with different deuteration strategies.
3. The four basic steps are monochromation, collimation, scattering and detection.
4. SANS uses scattering angles between 0.2 º and 20 º in two steps.
5. In-situ SANS environments include: shear cells/rheometers, pressure cells, electromagnets/superconducting magnets, humidity cells, etc.
6. SANS research areas include: polymers, complex fluids, biology, materials science, magnetism, etc.
7. SANS instruments are bigger than SAXS instruments because of the inherently lower flux neutron sources. Neutron current on sample is increased for SANS instruments by making larger samples. Larger samples imply longer SANS instruments in order to cover the same Q range.